Comment on "Adsorption of C60 on Ta(110)

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Comment on "Adsorption of C_{60} on Ta(110): Photoemission and C K-edge studies"

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In a recent paper [Phys. Rev. B **48**, 15 457 (1993)] Ruckman *et al.* characterized ultrathin C_{60} films on a Ta(110) surface by photoemission and C K-edge studies. They concluded that some fraction of the fullerene overlayer decomposes on the clean metal surface resulting in a thin layer of carbon between the assembled film and the metal substrate. In this Comment we argue that there is not enough experimental evidence to sustain this interpretation. Their experimental results can be interpreted by a chemisorbed first monolayer without inferring the formation of a thin carbon layer at the interface. Furthermore, their proposed alignment of the C_{60} π and π^* energy levels is not correct.

I. INTRODUCTION

In a recent paper Ruckman, Xia, and Qiu[1] have studied the interaction of C_{60} with Ta(110) from submonolayer up to multilayer coverages. Their conclusion that "some of the C_{60} decomposes to form an atomically thin carbon layer between the fullerenes and the metal" is based on (a) the absence of typical C_{60} emission bands in the ultraviolet photoemission spectroscopy (UPS) spectra for coverages lower than 0.4 ML; (b) a two-component fit of the C 1s line of the C_{60} monolayer; and (c) the broadening and apparent decrease of the surface component of the Ta 4f line for one adsorbed monolayer of C_{60}. The aim of this Comment is to show that there is not sufficient experimental evidence to conclude on a decomposition of C_{60} on Ta(110) and to show that their proposed energy-level diagram for the C_{60}/Ta(110) interface is wrong. Their experimental observations can indeed be explained in a very simple way by a chemisorbed first monolayer and a charge transfer from the substrate to the first layer C_{60} like for many other C_{60}-metal[2-6] or -semiconductor[7] interfaces.

II. C_{60} DECOMPOSITION ON Ta(110)

The films used by Ruckman, Xia, and Qiu in their study are obtained by subliming a C_{60}/C_{70} mixture on the Ta(110) substrate *at room temperature.* These deposition conditions favor island growth mode and for a nominal coverage of 1 ML of C_{60} parts of the Ta surface will still be bare while others will be covered by multilayer C_{60} islands. Indeed no scanning tunneling microscopy (STM) (Refs. 6–18) or x-ray photoemission study[3,4,19] performed so far on metal and semiconductor surfaces has reported a layer-by-layer growth for room-temperature C_{60} deposition. Even on rather inert and weakly interacting lamellar compounds, which should favor layer-by-layer growth, island growth has been reported at room temperature.[20] In addition Ruckman, Xia, and Qiu refer to the C_{60} ML as a "single close-packed layer," but do not report on any structural investigation. We argue that the C_{60}/Ta(110) film is probably not epitaxial and that different adsorption sites might be possible for C_{60} on the Ta(110) surface. For systems where the first monolayer is chemisorbed, as for the system under investigation, epitaxial growth has indeed only been achieved when the substrate was heated to or above 200 °C during evaporation.[3-18] The influence of the substrate temperature on the crystallinity of the C_{60} film has been demonstrated by several studies on metal,[3-6,12-18] semiconductor,[7-11] and even lamellar substrates.[21-25] Furthermore, Ruckman, Xia, and Qiu do not explain how they calibrated the C_{60} coverage but only mention that the coverages were estimated from the attenuation of the Ta 4f line, a method which cannot be very accurate for the system under discussion. If one takes this into account and also considers the high cross section for the Ta 5d line, it is not surprising that with the resolution (0.4 eV) and the statistics of the data presented no typical C_{60} valence-band features are observed in the 0.1-ML spectrum. The eventual C_{60} features of the lowest coverage spectrum might fall within the noise level. The absence of any *sharp* C_{60} line in the 0.1-ML spectrum gives therefore no evidence for a (graphitic) carbon layer at the interface which would be characterized by *broad* energy bands in the UV spectrum and which are not observed.

Their second argument in favor of a decomposition of C_{60} at the interface is based on a line-shape analysis of the C 1s line. The C 1s line for a thick layer is located at 285.5 eV (somewhat higher than the values reported in the literature for C_{60}-metal interfaces)[2-4] and has a width of about 1.6 eV (their energy resolution is at least 1 eV). For the monolayer they observe an additional broadening of about 0.4 eV and a shift of 0.7 eV which is in good agreement with that observed for other C_{60}-metal interfaces.[2-4] According to the authors the C 1s line of the 1-ML spectrum "can be fitted with a single broad peak *or* two peaks." They do not give any argument why they prefer the two-component fit to interpret their spectrum. We argue that anyway there will be several nonequivalent carbon atoms at the interface: (1) for C_{60} molecules in direct contact with the substrate the charge transferred

from the substrate might not be distributed evenly over the whole molecule; (2) not all the molecules in contact with the metal surface have the same surrounding (different adsorption sites, domain boundaries, etc.); (3) due to the island growth there will be a contribution from second- and third-layer C_{60} which will be much less affected by the charge transfer. In addition to that, there will be a broadening on the higher binding energy side for the chemisorbed molecules which is mainly due to the creation of electron-hole pairs in the partially filled band formed at the interface.[4] These arguments are sufficient to explain the shape of the C 1*s* line of the monolayer without inferring the existence of a thin carbon layer at the interface.

Concerning the Ta 4*f* doublet, the authors fit their spectrum of 1-ML C_{60}/Ta(110) with three doublets. It is evident, as seen from the statistics of the data, that their fit does not match the experimental spectrum. Furthermore, the physical origin of the three components is not clear in their discussion. In fact, if the surface were covered by a carbon layer or a TaC at the interface, there is no reason why there should be more than two components. If instead, one considers island growth of C_{60} without decomposition of C_{60}, it is obvious that Ta atoms with different surroundings would contribute to the Ta 4*f* signal: (1) bulk Ta; (2) bare Ta surface atoms surrounded by Ta atoms; and (3) Ta atoms in contact with chemisorbed C_{60}. The broadening and the shift of the Ta 4*f* line after C_{60} adsorption can therefore be explained again without considering the formation of a thin carbon layer at the interface.

Other arguments against a decomposition are the extremely high stability of C_{60} (Ref. 26) and the fact that no investigation of the electronic and vibrational properties of C_{60} adsorbed on noble[2–4,27,28] and transition[2,5] metal or semiconductor[2,19] surfaces has found evidence for C_{60} decomposition at room temperature. Why should the interaction of C_{60} with Ta be that different from that with other transition metals, for example, Rh,[5]Cr, [2]Mo, [29] or Ni?[30]

III. ENERGY LEVEL ALIGNMENT

Based on the measured position of the highest occupied molecular orbital (HOMO) in the valence-band spectra recorded for a thick C_{60} layer, on a band gap of 1.6 eV, and on the measurement of the work function of Ta and its increase upon adsorption of 1-ML C_{60} (0.6 eV) the authors draw a diagram of the alignment of the C_{60} HOMO and lowest unoccupied molecular orbital (LUMO) levels with the Ta valence band in which the LUMO level is placed below the Fermi level. According to this picture the LUMO should then be fully occupied (charge transfer of six electrons from the substrate) and give rise to an additional peak in the valence band which is neither observed nor discussed.

There are several problems with their reasoning. For bulk C_{60}, the energy position of the HOMO and its relative intensity compared to the HOMO-1, in contrast with the authors' affirmation, do not match those published in the literature.[31] Indeed their measured HOMO position is 1.72 eV while the commonly accepted value is 2.1–2.3 eV.[32,33] Moreover, one should consider that the HOMO-LUMO separation as determined by combined direct and inverse photoemission measurements (3.5 eV) (Ref. 32 and 33) does not correspond to the fundamental gap [1.6–1.9 eV (Ref. 35)] because of electron correlation effects.[32–34] The HOMO position is therefore closer to the Fermi level than the HOMO-derived feature observed in the experimental spectrum. The correct energy-level picture should be the following: (1) for the monolayer, the LUMO will be placed just *above* the Fermi level with a tail extending below E_F, as a consequence of the charge transfer from the substrate to the C_{60} molecules (in agreement with the observed work function change); (2) for the thick layer, the C_{60} energy levels are simply referenced to the vacuum level. This picture implies that energy shifts should be observed in the valence-band structures on going from submonolayer coverages to the thick overlayer. Despite the authors' affirmation that "little or no shift in position" is observed for all structures below the HOMO-1 level, one can clearly see that these peaks shift by about 0.9 eV to higher binding energies with increasing coverage. This shift, which is characteristic of chemisorptive adsorption of the first monolayer, is of the same order of magnitude as the one observed for benzene on transition metals[36] and for C_{60} on Au(110).[4]

IV. CONCLUSION

In this Comment we have shown that the x-ray photoemission spectroscopy and UPS spectra reported by Ruckman, Xia, and Qiu on the C_{60}/Ta(110) interface show no conclusive evidence for a decomposition of C_{60} and a formation of a thin carbon layer. Their data can be very simply explained by a chemisorbed first monolayer with charge transfer from the substrate, similar to what has been observed for C_{60} on other metals and semiconductors. We have also pointed out that the alignment of the C_{60} π and π^* levels proposed by Ruckman, Xia, and Qiu is not correct.

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[1]M. W. Ruckman, B. Xia, and S. L. Qiu, Phys. Rev. B **48**, 15 457 (1993).

[2]T. R. Ohno Y. Chen, S. E. Harvey, G. H. Kroll, J. H. Weaver, R. E. Haufler, and R. E. Smalley, Phys. Rev. B **44**, 13 747 (1991).

[3]J. E. Rowe, P. Rudolf, L. H. Tjeng, R. A. Malic, G. Meigs, C. T. Chen, J. Chen, and E. W. Plummer, Int. J. Mod. Phys. B **6**, 3909 (1992).

[4]A. J. Maxwell, P. A. Brühwiler, A. Nilsson, N. Martensson, and P. Rudolf, Phys. Rev. B **49**, 10 717 (1994).
[5]A. Sellidj and B. E. Koel, J. Phys. Chem. **97**, 10 076 (1993).
[6]Y. Kuk, D. K. Kim, Y. D. Suh, K. H. Park, H. P. Noh, S. J. Oh, and S. K. Kim, Phys. Rev. Lett. **70**, 1948 (1993).
[7]X.-D. Wang, T. Hashizume, H. Shinohara, Y. Saito, Y. Nishina, and T. Sakurai, Phys. Rev. B **47**, 15 923 (1993).
[8]Y. Z. Li, J. C. Patrin, M. Chander, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, Phys. Rev. B **45**, 13 837 (1992).
[9]Y. Z. Li, J. C. Patrin, M. Chander, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, Science **252**, 547 (1991).
[10]J. H. Weaver, Acc. Chem. Res. **25**, 143 (1992).
[11]H. Xu, D. M. Chen, and W. N. Creager, Phys. Rev. Lett. **70**, 1850 (1993).
[12]R. J. Wilson, G. Meijer, D. S. Bethune, R. D. Johnson, D. D. Chambliss, M. S. de Vries, H. E. Hunziker, and H. R. Wendt, Nature **348**, 621 (1990).
[13]J. L. Wragg, J. E. Chamberlain, H. W. White, W. Krätschmer, and D. R. Huffman, Nature **348**, 623 (1990).
[14]T. Hashizume, X. D. Wang, Y. Nishina, H. Shinohara, Y. Saito, Y. Kuk, and T. Sakurai, Jpn. J. Appl. Phys. **31**, L880 (1992).
[15]T. Hashizume, K. Motai, X. D. Wang, H. Shinohara, Y. Saito, Y. Maruyama, K. Ohno, Y. Kawazoe, Y. Nishina, H. W. Pickering, Y. Kuk, and T. Sakurai, Phys. Rev. Lett. **71**, 2959 (1993).
[16]H. Yu, J. Yan, Yanfang Li, W. S. Yang, Z. Gu, and Y. Wu, Surf. Sci. **286**, 116 (1993).
[17]E. I. Altman and R. J. Colton, Surf. Sci. **279**, 49 (1992).
[18]J. K. Gimzewski, S. Modesti, Ch. Gerber, and R. R. Schlittler, Chem. Phys. Lett. **213**, 401 (1993).
[19]G. Gensterblum, K. Hevesi, B.-Y. Han, L.-M. Yu, J.-J. Pireaux, P. A. Thiry, R. Caudano, A.-A. Lucas, D. Bernaerts, S. Amelinckx, G. Van Tendeloo, G. Bendele, T. Buslaps, R. L. Johnson, M. Foss, R. Feidenhans'l, and G. Le Lay, Phys. Rev. B (to be published).
[20]H. G. Busmann, R. Hiss, H. Gaber, and I. V. Hertel, Surf. Sci. **289**, 381 (1993).
[21]G. Gensterblum, L-M. Yu, J.-J. Pireaux, P. A. Thiry, R. Caudano, J.-M. Themlin, S. Bouzidi, F. Coletti, and J.-M. Debever, Appl. Phys. A **56**, 175 (1993); J.-M. Themlin, S. Bouzidi, F. Coletti, J.-M. Debever, G. Gensterblum, L.-M. Yu, J.-J. Pireaux, and P. A. Thiry, Phys. Rev. B **46**, 15 602 (1992).
[22]W. Krakow, N. M. Rivera, R. A. Roy, R. S. Ruoff, and J. J. Cuomo, Appl. Phys. A **56**, 185 (1993).
[23]J. E. Fischer, E. Werwa, and P. A. Heiney, Appl. Phys. A **56**, 193 (1993).
[24]G. Gensterblum, L.-M. Yu, J.-J. Pireaux, R. Caudano, Ph. Lambin, A. A. Lucas, W. Krätschmer, and J. E. Fischer, J. Phys. Chem. Solids **53**, 1427 (1992).
[25]M. Sakurai, H. Tada, K. Saiki, A. Koma, H. Funasaka, and Y. Kishimoto, Chem. Phys. Lett. **208**, 425 (1993).
[26]D. R. Huffman, Phys. Today **44** (11), 22 (1991); J. Aihara, Sci. Am. **1992** (3), 44; J. R. Chelikowsky, Phys. Rev. Lett. **67**, 2970 (1991).
[27]S. Modesti, S. Cerasari, and P. Rudolf, Phys. Rev. Lett. **71**, 2469 (1993); R. L. Garell, T. M. Herne, C. A. Szafranski, F. Diederich, F. Ettl, and R. L. Whetten, J. Am. Chem. Soc. **113**, 6302 (1991).
[28]K. L. Akers, L. M. Cousins, and M. Moskovits, Chem. Phys. Lett. **190**, 614 (1992).
[29]P. A. Brühwiler (private communication).
[30]M. H. Hunt, P. Rudolf, and S. Modesti (unpublished); A. K. Santra, R. Seshadri, V. Vijayakrishnan, and C. N. R. Rao, Solid State Commun. **85**, 77 (1993).
[31]P. J. Benning, D. M. Poirier, N. Troullier, J. L. Martins, J. H. Weaver, R. E. Haufler, L. P. F. Chibante, and R. E. Smalley, Phys. Rev. B **44**, 1962 (1991).
[32]R. W. Lof, M. A. van Veenendaal, B. Koopmans, H. T. Jonkman, and G. A. Sawatzky, Phys. Rev. Lett. **68**, 3924 (1992).
[33]J. H. Weaver, J. Phys. Chem. Solids **53**, 1433 (1992).
[34]S. Krummacher, M. Biermann, M. Neeb, A. Liebsch, and W. Eberhardt, Phys. Rev. B **48**, 8424 (1993); P. A. Brühwiler, A. J. Maxwell, P. Rudolf, C. D. Gutleben, B. Wästberg, and N. Martenson, Phys. Rev. Lett. **71**, 3721 (1993).
[35]S. Saito and A. Oshiyama, Phys. Rev. Lett. **66**, 2637 (1991); N. Troullier and J. L. Martins, Phys. Rev. B **46**, 1754 (1992); E. L. Shirley and S. G. Louie, Phys. Rev. Lett. **71**, 133 (1993).
[36]C. M. Mate, C. T. Kao, and G. A. Somorjai, Surf. Sci. **206**, 145 (1988); E. W. Plummer, W. R. Salaneck, and J. S. Miller, Phys. Rev. B **18**, 1673 (1978); B. Gumhalter, K. Wandelt, and Ph. Avouris, *ibid.* **37**, 8048 (1988).